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HYDROGENATION AND DEHYDROGENATION OF HYDROCARBONS
IN CONTACT WITH CATALYSTS CONTAINING LOW PERCENTAGES OF NICKEL

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[Table and figures are appended.]

[The work in question represents an attempt to develop efficient hydrogenation and dehydrogenation procedure in a type of conversion which is of great importance in fuel and petroleum technology, and to effect at the same time a considerable saving of nickel, thus lowering the cost of the product, simplifying problems in connection with the recovery of the catalyst, and making available an increased supply of nickel for other uses.]

Previous investigations [1] by this group of scientists on the hydrogenation of benzene, alkenes, and cyclenes, and the dehydrogenation of cyclohexane in the presence of platinated carbon with a very small percentage of platinum showed that catalysts with a low percentage of platinum can be used widely in the hydrogenation of unsaturated hydrocarbons and the dehydrogenation of six-membered cyclanes.

Through the work of N.D. Zelinskiy and his collaborators [2], nickel catalysts on various carriers (aluminum oxide, silica gel, and activated carbon) have become widely used for hydrogenation and dehydrogenation catalysis. However, the nickel catalysts used so far have had a high percentage of the nickel itself -- up to 50% [3].

In studying the scientific basis for the selection of catalysts, this group of investigators set out to determine the hydrogenating and dehydrogenating properties of a series of nickel catalysts with small nickel content.

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To carry out this investigation, six specimens of nickel on activated carbon -- with the contents of nickel varying from 0.125% to 4% -- were prepared under precisely the same conditions, except that the concentration of the solution of nickel nitrate was varied in each case. All of the catalysts were prepared by impregnating activated birch charcoal with the nickel nitrate solution at 30-35°. In all cases, 2 ml of solution per gram of dry carbon were used. The carbon was steeped in the solution at 40-45°, after which the catalysts were dried at 125° to a constant weight. Reduction of the catalysts was accomplished by subjecting them to a current of electrolytic hydrogen at 330° until the liberation of the nitrogen oxides ceased.

The experiments were conducted in an ordinary apparatus of the circulating type. Hydrogenation of benzene was carried out in an excess current of hydrogen in the temperature range of 115-176° at a volume velocity of 0.025-0.2 l/l of the catalyst per hr. Dehydrogenation of cyclohexane was carried out in a weak current of hydrogen at 300-302° and the exchange velocity 0.2 l/l of the catalyst per hr. The degree of conversion of benzene into cyclohexane, as well as of the latter into benzene, was controlled with a refractometer [5].

Table 1 shows the results of the determination of the initial activity of catalysts in the hydrogenation of benzene and the dehydrogenation of cyclohexane. These tests were conducted at constant volume velocities.

This data shows that the hydrogenation of benzene proceeds to a considerable degree for catalysts with a nickel content greater than 1%. Catalysts containing less than 0.5% nickel also have the ability to hydrogenate a benzene ring, although to a lesser degree than the platinated catalysts with a similar metal content [1].

The initial dehydrogenating activity of the nickel catalysts with nickel content from 0.5 to 4% varies very little, although it is not very high even for the 4% catalyst. The variation in the activity of catalysts containing 4 and 2% nickel in relation to the duration of their activity in the dehydrogenation of cyclohexane is shown in Figure 1.

As can be seen from this figure, 2,000 min after the beginning of the experiment, the activity of these catalysts is reduced by a factor of 3-4. Therefore, the dehydrogenating ability of the catalysts under continuous operation conditions drops rather rapidly.

Catalysts with 2 and 4% nickel content exhibit good activity in the hydrogenation of benzene at various temperatures and volume velocities, as seen in Figure 2 in the exchange velocity. Variation of temperature between 120 and 176° does not for practical purposes change the degree of conversion of benzene, which under these conditions is 100%. Furthermore, an eightfold increase in the volume velocity reduces the degree of conversion of benzene only to 68-70%.

Figure 3 shows the change in the activity of the catalyst with respect to time in the hydrogenation of benzene with a volume velocity of 0.06 l/l of the catalyst per hr.

As shown by the curves in Figure 3, the degree of conversion of benzene into cyclohexane in the course of more than 25 hr is close to 100% for the 4% catalyst.

These experiments, then, give a basis for recommending 2 and 4% nickel catalysts on activated carbon for use in laboratory practice in the vapor-phase hydrogenation of the benzene ring.

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Table 1*

No of Catalyst	Ni (in %)	Benzene			Cyclohexane	
		Amt of Ni in Catalyst (in g)	n_D^{20} Catalyzate	% of Conversion	n_D^{20} Catalyzate	% of Conversion
1	4	0.880	1.4263	100	1.4478	37.8
2	2	0.430	1.4265	100	1.4445	32.2
3	1	0.202	1.4360	82.0	1.4427	29.2
4	0.5	0.104	1.4596	46.4	1.4410	26.6
5	0.25	0.049	1.4789	24.6	1.4370	19.8
6	0.125	0.024	1.4896	11.4	1.4330	12.0

*Volume velocity of benzene = 0.04 l/l of catalyst per hr

Temperature of hydrogenation = 186°C

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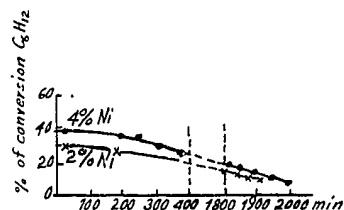


Figure 1. Change in the Activity of Catalyst under Conditions of Cyclohexane Dehydrogenation (volume velocity 0.2 l/l of the catalyst per hr)

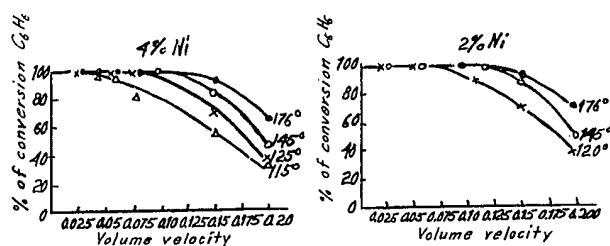


Figure 2. Hydrogenation of Benzene

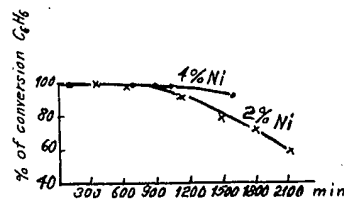


Figure 3. Change in the Activity of Catalysts Under Conditions of Benzene Hydrogenation (volume velocity 0.06 l/l of the catalyst per hr)

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